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MEASUREMENTS OF GAS-PHASE REACTION RATES INVOLVING N2O AND CH2O--ETC(U)

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Rate constants have been determined from shock-tube observations,
in the interval $1685 \leq T, ^\circ K \leq 2560$, for the following elementary reaction
steps: $N_2O + M \rightarrow N_2 + O + M$, $N_2O + O \rightarrow 2NO$, and $N_2O + O \rightarrow N_2 + O_2$.DD FORM 1473
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1. Publications

The following papers have been submitted for publication (see the attached copies of the manuscripts): (a) K. G. P. Sulzmann, J. M. Kline and S. S. Penner, "Shock-Tube Studies of N₂O-Decomposition," Twelfth International Symposium on Shock Tubes & Waves, Technion, Israel Institute of Technology/The Hebrew University of Jerusalem, Jerusalem, Israel, 1979. (b) K.G.P. Sulzmann, J. M. Kline and S. S. Penner, "Empirical Determinations of the Effective Absorption Coefficients for the NO γ -Bands at 2259 A and the ν_3 -Fundamental of N₂O at 4.52 μ ," JQSRT, in press (1979).

2. Experimental Accomplishments

We have completed thermal decomposition studies¹ on nitrous oxide behind reflected shock waves for $1685 \leq T, ^\circ K \leq 2560$ and $1.7 \leq p, \text{ atm} \leq 4.6$ in N₂O-Ar

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mixtures containing 2% N_2O . Concentration-time histories have been determined for N_2O from absolute emission intensities at 4.52μ ($\Delta\lambda = 0.083 \mu$) and for NO by absolute correlation-absorption spectroscopy at 2259 \AA ($\Delta\lambda = 39 \text{ \AA}$). The needed spectral absorption coefficients were obtained by the use of semi-empirical procedures (see below).

Our studies revealed that there is some delay before the O-atom concentrations attain a steady state at low temperatures at which the initial N_2O -decomposition is governed by the binary decomposition reaction $\text{N}_2\text{O} + \text{M} \xrightarrow{k_1} \text{N}_2 + \text{O} + \text{M}$. At the higher temperatures used, the reactions $\text{N}_2\text{O} + \text{O} \xrightarrow{k_2} 2\text{NO}$ and $\text{N}_2\text{O} + \text{O} \xrightarrow{k_3} \text{N}_2 + \text{O}_2$ occur sufficiently rapidly for the O-atoms to attain steady-state concentrations (within the experimentally achieved time resolution) immediately after reflected shock-heating. When a steady state obtains for the O-atom concentration, the effective initial rate of N_2O -decomposition is double that for the one-step binary decomposition path ($2k_1$).

Data obtained for the initial slopes of N_2O -disappearance at the lower temperatures, as well as from observed N_2O -decomposition rates at higher temperatures when steady-state conditions for the O-atom concentrations are reached, lead directly to the value ($1685 \leq T, ^\circ\text{K} \leq 2560$)

$$k_1 = (3.71 \pm 2.74) \times 10^{14} \exp[-(27,660 \pm 1,445)^\circ\text{K}/T] \text{cm}^3/\text{mole-sec},$$

in close agreement with recent, indirect estimates derived by computer fits to experimental data.^{2,3}

Straightforward integrations of the rate equations lead to analytical expressions for (N_2O) , (NO) and (O) as functions of $x = \int_0^t (\text{N}_2\text{O}) dt'$; these show that values for k_1 , k_2/k_3 and $k_2 + k_3$ are determined independently from (N_2O) and (NO) time-histories; values for k_1 and k_2/k_3 are measurable over the entire temperature range employed, regardless of whether or not the O-atoms are at the steady state initially. Analysis of the concentration time-histories for (N_2O) and (NO) show that $k_3/k_2 = 1.09 \pm 0.10$ for $1685 \leq T, ^\circ\text{K} \leq 2560$, in close agreement with the usual assumption $k_2 = k_3$ made in the review by Baulch et al.⁴ Values for $k_2 + k_3$ could be determined from (N_2O) - or (NO) -histories when the O-atom concentration did not reach a steady-state value immediately after shock heating ($T \leq 2000^\circ\text{K}$). We have obtained the explicit relations ($1685 \leq T, ^\circ\text{K} \leq 2000$)

$$k_2 = (4.07 \pm 3.26) \times 10^{13} \exp[-(12,350 \pm 2,380)^\circ\text{K}/T] \text{cm}^3/\text{mole-sec}$$

and

$$k_3 = (4.43 \pm 3.97) \times 10^{13} \exp[-(12,350 \pm 2,380)^\circ\text{K}/T] \text{cm}^3/\text{mole-sec}.$$

Although our activation energy for k_2 and k_3 agrees nearly with those given in Refs. 2 and 3, our data fall more closely on the expression adopted for k_2 in the cited review.⁴

Measurements of the concentration time-histories for NO and N_2O were accomplished by absolute correlation-absorption spectrometry in the NO γ -bands and by absolute emission-spectroscopy in the N_2O ν_3 -fundamental regions.

For this purpose, shock-tube correlation-absorption data for NO at 2259 Å ($\Delta\lambda = 39$ Å) of low-pressure (~ 5 torr) emission lines by high-pressure ($0.5 \leq p$, atm ≤ 2.1) and high-temperature ($905 \leq T$, °K ≤ 2015) lines belonging to the (0,0) band of the NO γ -system were obtained by using an effective absorption coefficient for emission lines of negligible width and line-center absorption by isolated Voigt-lines of a common width.⁵ The band f-number required for this model was found to differ by - 26% from the preferred value. Modelling the system by narrow-line emission and absorption by a just-overlapping band system did not correlate the observed data.

The shock-tube emission data at 4.52μ ($\Delta\lambda = 0.083 \mu$) for N₂O in the ν_3 -fundamental were calibrated for $975 \leq T$, °K ≤ 2300 and $0.4 \leq p$, atm ≤ 2.2 and could be well described by the just-overlapping line model. The resultant integrated band-intensity agreed within 9.4% with recent literature data.⁵

3. Experimental Facilities

The ultraviolet absorption-photometer for absolute correlation absorption-spectroscopy has been modified for measurements in the vacuum ultraviolet of O-atom concentrations near 1305 Å or for H-atom concentrations near 1215 Å. For this purpose, a new EMI-G26E315/R1 solar-blind, vacuum-ultraviolet photomultiplier with CsI-cathode and MgF₂-window has been installed in the system. An oil-diffusion pump and a liquid nitrogen cold-trap have been attached to the vacuum-sealed optical path of the photometer

system. The system can be evacuated routinely to 10^{-4} torr, which suppresses absorption losses by air (mainly O_2) to less than 0.6% at the wavelengths of interest. The construction of an apparatus for the preparation of pure formaldehyde from paraformaldehyde is completed. This system allows paraformaldehyde to be heated to 100°C and the resulting monomeric CH_2O to be repeatedly vacuum-distilled by condensing it at liquid nitrogen temperature (-196°C) from an evaporation chamber at the temperature of acetone/dry ice (-77°C). The resulting pure formaldehyde will be mixed quasi-statically with argon-diluted test gases of N_2O by a dynamic mixing procedure⁶⁻⁸ in order to avoid mixing errors caused by wall adsorption and/or desorption associated with conventional static procedures using partial pressures.

We have completed the adaptation of the NASA chemical-kinetics computer code¹⁰ (NASA N62-1526) to our computer facilities. We have added to the code an option for generating chemical kinetics-histories near the end-plate behind reflected shock-waves at constant density and at constant specific enthalpy. These conditions are valid for reacting gases behind reflected shock-waves if the heat released (or consumed) by the reactions does not influence the (steady) shock propagation, i.e., for highly diluted reacting mixtures. This code will enable us in the future to generate synthetic species-concentration histories for comparisons with experimental measurements behind incident and reflected shock-waves.

4. Relation of the UCSD program to A. M. Dean's Work

Although Dean's group has experimented with the synthesis of monomeric formaldehyde, we have some questions concerning the validity of the mixing procedure using partial pressures without utilizing the vapor pressure as a function of temperature for condensed formaldehyde. Because we have found that large errors were introduced by wall adsorption and desorption when metering low-concentrations, we have adopted in the past a dynamic (quasi-static) mixing procedure (see above) which avoids these problems.

Dean's group is currently studying reactions of CH_2O with H-atoms, O-atoms, and OH-radicals and will also investigate interactions of CH_3 with O_2 and O-atoms as well as interactions of HCN and NH_3 with O-atoms. These studies constitute steps in the direction of necessary kinetics measurements on simplified chemical systems that relate to the much more complex combustion chemistry encountered with species such as CH_4 and other hydrocarbons.

The rationale and need for these types of studies have been emphasized by us in the past in conjunction with CH_4 -oxidation investigations.¹¹ Our continuing studies on shock-heated, Ar-diluted, $\text{H}_2\text{CO-N}_2\text{O}$ -mixtures are part of this rationale and are designed to determine kinetic parameters for the mechanisms governing the interactions of atomic oxygen with H_2CO by

utilizing the potential of our existing spectrophotometric systems. The experimental facilities available to us for these investigations involve the following:

(a) two infrared spectrophotometers for quantitative emission measurements between 0.85 and 8.5 μ ; (b) a multi-chromator photometer system for up to twelve simultaneous absolute emission measurements in the ultraviolet and visible regions of the spectrum (~ 2600 A to 8000 A); (c) an ultraviolet and vacuum-ultraviolet, correlation-absorption spectrophotometer for absolute absorption measurements between 1200 and 3500 A; (d) selected lasers for laser-absorption measurements. We are able to accommodate in each test run two infrared-emission measurements, together with an ultraviolet absorption measurement and up to twelve ultraviolet/visible emission measurements. When necessary, an absolute laser-absorption measurement^{6, 12} may be performed.

In our current studies on the $\text{H}_2\text{CO-N}_2\text{O}$ system, we make use of combinations of four of the following types of spectral measurements (two IR-emissions, one UV-absorption and one UV-emission):

Infrared emission

- (a) H_2CO -emission near 3.48 μ and/or 5.73 μ ;
- (b) N_2O -emission near 4.52 μ and/or 7.78 μ ;
- (c) CO-emission near 4.80 μ ;
- (d) NO-emission near 5.30 μ ;

(e) CO_2 -emission near 4.25μ ;

(f) H_2O -emission near 2.57μ .

Ultraviolet and vacuum ultraviolet absorption

(g) H-absorption near 1215 A;

(h) O-absorption near 1305 A;

(i) NO-absorption near 2262 A;

(j) H_2CO -absorption near 3164 A or 2931 or 2839 A;

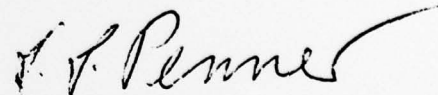
(k) O_2 -absorption near 2226 A.

Visible and ultraviolet emission

(l) CO-O-emission near 3700 A.

Duplication of species monitoring in different spectral channels will be used, whenever necessary, in order to eliminate ambiguities caused by band-overlap of different radiators.

Submitted by



S. S. Penner

Principal Investigator

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K. G. P. Sulzmann

Co-Principal Investigator

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